REACTION OF 4-METHYL-3,4-EPOXYTETRAHYDROPYRAN WITH GRIGNARD REAGENTS WITH ISOMERIZATION TO TETRAHYDROFURAN DERIVATIVES

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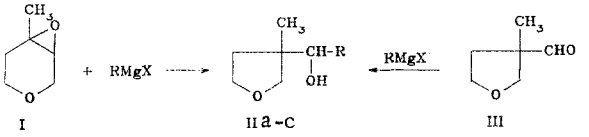
We have shown that the reaction of 4-methyl-3,4-epoxytetrahydropyran (I) with Grignard reagents is accompanied by isomerization, which leads to tetrahydrofuran derivatives II.



I IIa-c III

II a R=C_2H_5; b R=*i*-C_5H_{11}; c R=C_6H_5

This rearrangement is even more noteworthy in that it is the first example in the tetrahydropyran oxide series and among trisubstituted epoxides in general [2] of reactions with Grignard reagents that are accompanied by isomerization. The compounds obtained were identified from data from PMR spectroscopy and gas–liquid chromatography (GLC) and by alternative synthesis from 3-methyl-3-formyltetrahydrofuran (III) [3].

The reaction of 0.15 mole of the Grignard reagent and 0.1 mole of oxide I (or aldehyde III) in absolute ether at −10°C gave IIa [74% (75% from the aldehyde), bp 152-154°C (14 mm), n_D^{20} 1.4625, and d_4^{20} 1.0032], IIb [63% (71%), bp 100-101°C (3 mm), n_D^{20} 1.4625, and d_4^{20} 0.9601], and IIc [88% (86%), bp 145-147°C (4 mm), n_D^{20} 1.5450, and d_4^{20} 1.0978]. PMR spectrum of alcohol IIc (CCl_4): 0.83 and 0.85 (3H, s, CH_3), 4.35 (1H, s, CH), 2.95-3.74 [4H, m, $(CH_2)_2O$], 1.18-2.05 (2H, m, CH_2), and 7.18 ppm (5H, s, C_6H_5).

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